



Photocatalytic reduction of CO₂ using H₂ as reductant over ATaO₃ photocatalysts (A = Li, Na, K)

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ABSTRACT

ATaO₃ (A = Li, Na, K) compound oxides exhibit photocatalytic activity for the reduction of CO₂ in the presence of H₂. Only CO gas was generated over all samples under photoirradiation. The photocatalytic activity was higher in the order corresponding to KTaO₃, NaTaO₃ and LiTaO₃ (LiTaO₃ > NaTaO₃ > KTaO₃). The order of the photocatalytic activities was consistent with that of the E_g (optical gap) values. After 24 h of photoirradiation, the amount of evolved CO reached 0.42 $\mu\text{mol g}^{-1}$ over LiTaO₃. TPD experiments indicated that the broad peak which is assigned to chemisorbed CO₂ gas was observed at 573 K in the case of LiTaO₃. On the contrary, there was no peak in the spectra of NaTaO₃ and KTaO₃. The amount of evolved CO gas almost strongly depends on the amount of chemisorbed CO₂ in the case of ATaO₃ (A = Li, Na, K). In addition, the photocatalytic activity increased with increasing the calcination temperature of LiTaO₃. This means that a smooth charge separation in a LiTaO₃ photocatalyst and chemisorption of CO₂ on the surface contribute to effective reduction of CO₂ in the presence of H₂.

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1. Introduction

Recently, many countries that have approved the ratification of the Kyoto Protocol are enforcing strict regulations on carbon dioxide (CO₂) emission to meet international environmental standards. These countries are reducing CO₂ emission in many different ways, for example, by storage in the ground and sea, absorption into various functionalized materials, and large-scale forestation. However, it is important to develop the technique to chemically convert CO₂ into harmless compounds or other chemical products in the future. Chemical fixation of CO₂ in the presence of a heterogeneous photocatalyst is a promising method for converting it into other carbon sources such as carbon monoxide (CO), formaldehyde (HCHO), formic acid (HCOOH), methanol (CH₃OH), and methane (CH₄) [1]. In the 1980s, the effect of H₂O as a reductant on heterogeneous photocatalysts used for the photocatalytic reduction of CO₂ attracted considerable interest [2,3].

We have found that CO is generated as a result of the photocatalytic reduction of CO₂ in the presence of H₂ or CH₄ as a reductant over ZrO₂ [4–9], Rh/TiO₂ [10,11], MgO [12,13], and Ga₂O₃ [14]. With the exception of Rh/TiO₂, these solid materials exhibit the properties of solid base catalysts; therefore, CO₂ can be adsorbed on

the surface of these materials. We have insisted on the importance of CO₂ adsorption on the surface because this makes CO₂, which is a stable and linear molecule, into an active species which provides abundant reactivity for the photocatalytic reduction of CO₂. As mentioned above, it was reported that the photocatalytic reduction of CO₂ in the presence of H₂ proceeds over many simple oxides such as ZrO₂, MgO, and Ga₂O₃. However, there is no report that a compound oxide exhibits photocatalytic activity for the reduction of CO₂. In the field of water splitting, many compound oxides are known to function as an effective photocatalyst. Among them, Kudo et al. [15,16] reported that La doped NaTaO₃ shows incredible photocatalytic activity for overall water splitting. In this study, we first found that ATaO₃ (A = Li, Na, K) is a candidate of photocatalyst for the reduction of CO₂.

2. Experimental

ATaO₃ (A = Li, Na, K) samples used in this study were synthesized by a conventional solid state reaction (SSR) method. A stoichiometric mixture of Ta₂O₅ and A₂CO₃ (A = Li, Na, K) was calcinated at 1373 K for 20 h in the atmosphere in a programmable box furnace. A 5 mol% excess of A₂CO₃ (A = Li, Na, K) was used to counteract loss of alkali as an oxide vapor during the heating circle. X-ray diffraction pattern (XRD) of an ATaO₃ (A = Li, Na, K) photocatalyst was measured by a Rigaku Multi Flex powder X-ray diffractometer. Kr adsorption isotherm was obtained using a BELSORP 28SA-SP system supplied by the BEL Japan Inc. The specific

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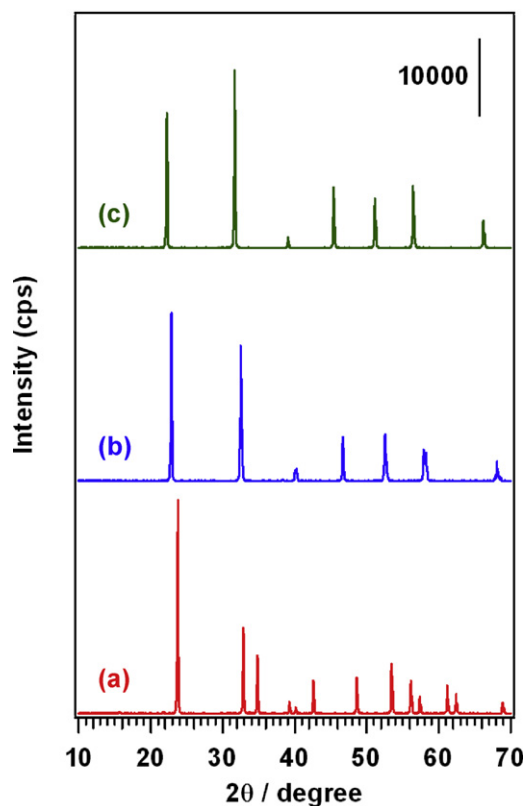


Fig. 1. XRD patterns of ATaO₃ (A = Li, Na, K): (a) LiTaO₃, (b) NaTaO₃ and (c) KTaO₃.

surface area was calculated from Kr adsorption isotherm of ATaO₃ (A = Li, Na, K) using the Brunauer–Emmett–Teller (BET) method because the specific surface area is too small to be estimated by N₂ adsorption isotherm. Scanning electron microscope (SEM) images were obtained on a Hitachi S-4700 scanning electron microscope. UV–vis diffuse reflectance (UV–vis DR) spectra were obtained using a JASCO Corporation V-670 diffused reflectance spectrometer with an integrating sphere at room temperature. BaSO₄ was used as a standard reflection sample. Temperature programmed desorption (TPD) profile was recorded by a TPD-1-AT instrument supplied by the BEL Japan Inc.

The photocatalytic reduction was carried out in a closed circulating system connected to a vacuum line. 2.0 g of ATaO₃ (A = Li, Na, K) was spread on the flat bottom (500) of a quartz reactor (dead space: 150 mL). The catalyst sample was heated and evacuated at 673 K and then treated with O₂ (80 kPa) for 60 min, followed by evacuation for 2 h at the same temperature. The purified CO₂ (150 μmol) as a substrate and H₂ (50 μmol) as a reductant were admitted to the reactor after the pretreatment. The ATaO₃ (A = Li, Na, K) sample was illuminated throughout a range of wavelength

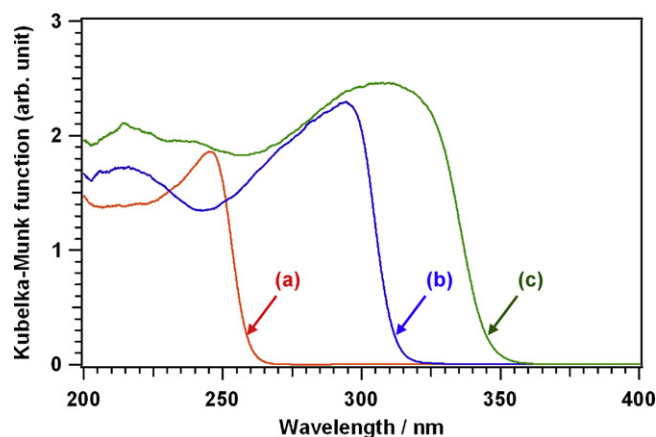


Fig. 3. UV–vis DR spectra of ATaO₃ (A = Li, Na, K): (a) LiTaO₃, (b) NaTaO₃ and (c) KTaO₃.

from the bottom of the reactor with a 200 W Hg–Xe lamp (SAN-EI ELECTRIC CO., LTD., UVF-204S Type C). The reaction temperature increased to 303 K after photoirradiation because of heat of the light source. The analysis of products was performed with TCD gas chromatograph (Shimadzu GC-8A) equipped with a column packed with active carbon and with helium (He) as a carrier gas.

3. Results and discussion

The prepared ATaO₃ (A = Li, Na, K) powders were qualitatively analyzed by some conventional method of analysis for a photocatalyst (XRD, SEM, and UV–vis spectroscopy). Fig. 1 shows the XRD patterns of ATaO₃ (A = Li, Na, K). The peak assigned to impurities did not appear in all XRD patterns. All of ATaO₃ consist of corner-sharing TaO₆ octahedra with ilmenite (LiTaO₃) and perovskite (NaTaO₃ and KTaO₃) like structures. The morphology of synthesized ATaO₃ (A = Li, Na, K) was observed by SEM as shown in Fig. 2. All prepared samples had fine primary particles with an average diameter of 1–3 μm. The BET specific surface areas of ATaO₃ (A = Li, Na, K) estimated by the Kr adsorption isotherm are 0.28, 0.10, and 0.10 m² g^{−1}, respectively. The UV–vis DR spectra of ATaO₃ (A = Li, Na, K) were obtained after converting reflection coefficient, R to $F(R_{\infty})$ by Kubelka–Munk function, $F(R_{\infty}) = (1 - R^2)/2R$ as shown in Fig. 3. Generally, E_g (optical gap) values are derived from optical absorption spectra and diffuse reflectance spectra. In the case of Davis–Mott's method, the E_g values are derived from the equation following $[F(R_{\infty}) \cdot h\nu] \propto (h\nu - E_g)^n$, where $n = 2, 3, 1/2$ and $3/2$ for indirect allowed, indirect forbidden, direct allowed, and direct forbidden transitions, respectively. The E_g values of ATaO₃ (A = Li, Na, K) are estimated to 4.9, 4.1 and 3.7 eV by Davis–Mott's method with $n = 1/2$ (direct allowed) [17,18].

Fig. 4 shows the amount of evolved CO gas for the photocatalytic reduction of CO₂ in the presence of H₂ as a reductant over ATaO₃

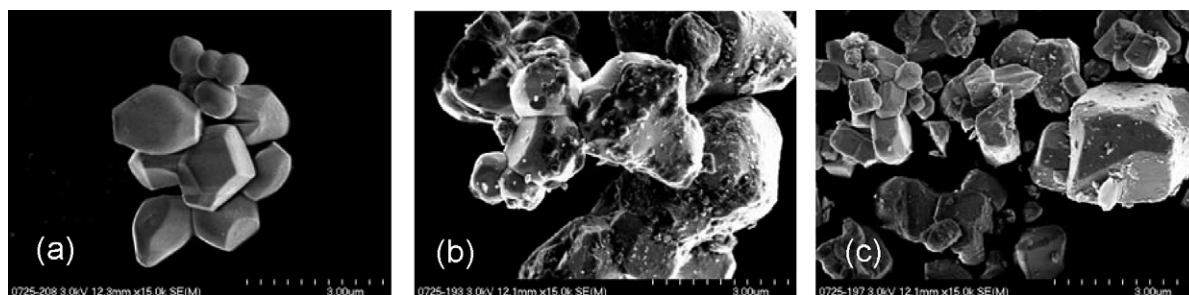


Fig. 2. SEM images of ATaO₃ (A = Li, Na, K): (a) LiTaO₃, (b) NaTaO₃ and (c) KTaO₃.

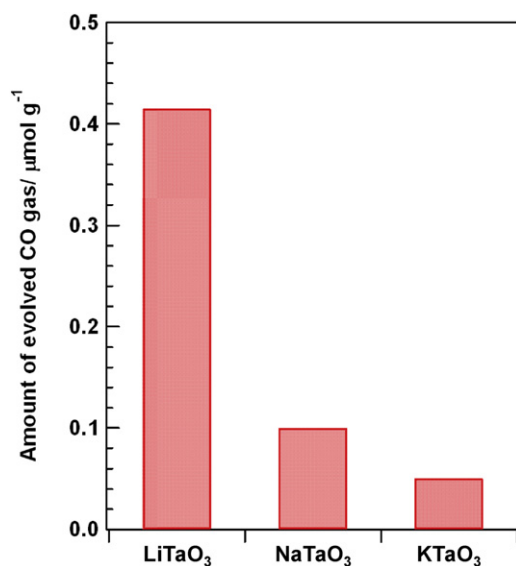


Fig. 4. Amount of evolved CO gas for the photocatalytic reduction of CO₂ in the presence of H₂ as a reductant over ATaO₃ (A = Li, Na, K) after 24 h of photoirradiation.

(A = Li, Na, K) after 24 h of photoirradiation. We obviously confirmed that the reaction does not proceed in the absence of ATaO₃ or in the dark. The photocatalytic reduction of CO₂ proceeded over all ATaO₃ (A = Li, Na, K) samples. CO gas was evolved over all ATaO₃ (A = Li, Na, K) samples under photoirradiation and the other compounds (for example, HCOOH, HCHO, CH₃OH, and CH₄) were not produced in the gas phase. LiTaO₃ exhibits the highest activity in the ATaO₃ (A = Li, Na, K) samples. The photocatalytic activity was higher in the order corresponding to KTaO₃, NaTaO₃ and LiTaO₃ (LiTaO₃ > NaTaO₃ > KTaO₃). Amount of evolved CO gas over LiTaO₃ was eight times higher than that over KTaO₃. No product was observed over LiTaO₃ under photoirradiation $\lambda > 310$ nm using a UV-29 cut-off filter. Therefore, the electron transition between band gap energy is concerned in the photocatalytic reduction of CO₂ over LiTaO₃. The order of the photocatalytic activities was consistent with that of the E_g (optical gap) values as described above. Kato and Kudo [15] concluded that the conduction band levels and the transferring excited energy contribute to photocatalytic activities of naked alkali tantalate photocatalysts and a surface area is not an important factor for overall water splitting because a LiTaO₃ photocatalyst showed the highest activity for overall water splitting among the naked alkali tantalate photocatalysts prepared in the presence of excess alkali and the order of the activities was LiTaO₃ > NaTaO₃ > KTaO₃. In our case, it is expected that the conduction band levels and the transferring excited energy influence the photocatalytic activity for the photocatalytic reduction of CO₂.

It was reported that solid base materials such as ZrO₂, MgO, CaO, Al₂O₃ and Ga₂O₃ which possess base sites on the surface exhibit photocatalytic activity for the photocatalytic reduction of CO₂ in the presence of H₂. CO₂ is adsorbed on the base site easily, and then the conformation of a linear CO₂ molecule undergoes a great change. The adsorption of CO₂ contributes to the photocatalytic reduction of CO₂. Fig. 5 shows the CO₂-TPD spectra ($m/z = 44$) of ATaO₃ (A = Li, Na, K) after pretreatment at 673 K and CO₂ adsorption at room temperature. A broad peak was observed at 573 K in the case of LiTaO₃, although there was no peak in the spectra of NaTaO₃ and KTaO₃. It is known that Li₂CO₃ is decomposed at 900 K (heat decomposition). In fact, we obtained the same result as the reference. Accordingly, the peak at 573 K is assigned to not decomposition of Li₂CO₃ but desorption of a CO₂ molecule adsorbed on LiTaO₃. The adsorption isotherm of CO₂ was observed after pretreatment at 673 K as shown in Fig. 6a. After that, CO₂ was adsorbed

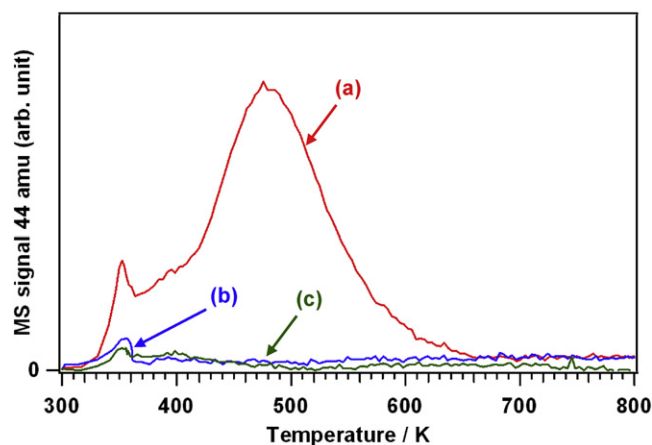


Fig. 5. CO₂-TPD spectra ($m/z = 44$) of ATaO₃ (A = Li, Na, K) after pretreatment at 673 K and CO₂ adsorption at room temperature.

on LiTaO₃ after evacuation at room temperature again as shown in Fig. 6b. These adsorption isotherms are expressed as a function of the Langmuir adsorption isotherm. Amount of adsorbed CO₂ was saturated when equilibrium pressure is more than 0.96 kPa. The subtraction between panels a and b was $0.75 \mu\text{mol g}^{-1}$. The equilibrium pressure was about 2.7 kPa when $150 \mu\text{mol}$ of CO₂ was admitted to the reactor with 2.0 g of LiTaO₃ after the pretreatment. Thus, the amount of CO₂ physisorbed and chemisorbed on LiTaO₃ corresponds to 2.76 and $1.50 \mu\text{mol}$ under the reaction condition, respectively. Fig. 7 demonstrates the amount of chemisorbed CO₂ on ATaO₃ (A = Li, Na, K). Amount of evolved CO gas almost depends on amount of chemisorbed CO₂ in the case of ATaO₃ (A = Li, Na, K) as well as the other reported materials such as ZrO₂, MgO, and Ga₂O₃.

We have reported that MgO exhibits the best photocatalytic activity for the reduction of CO₂ in the presence of H₂ as a reductant under UV light irradiation. It is clarified that the photoactive site of MgO is compatible with the CO₂ adsorption site. The amount of evolved CO gas over MgO ($12.9 \mu\text{mol g}^{-1}$) is thirty-first higher than that over LiTaO₃ ($0.42 \mu\text{mol g}^{-1}$) under 24 h of photoirradiation using the same light source. On the other hand, amount of

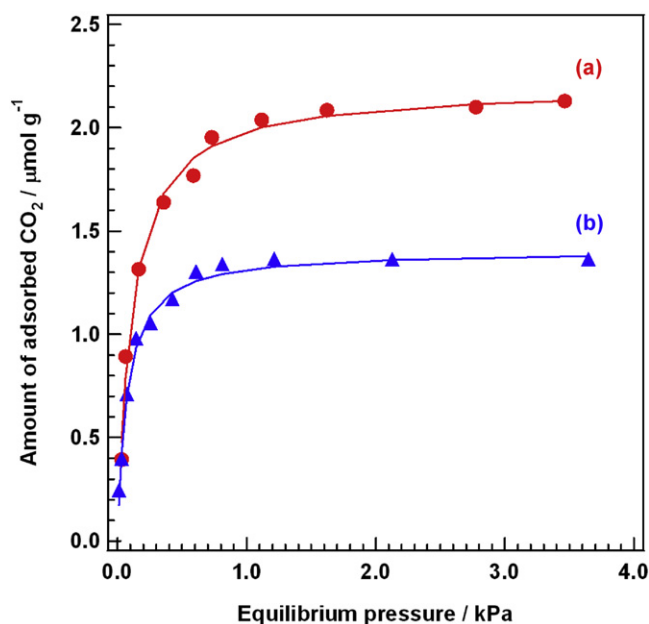


Fig. 6. The adsorption isotherms of CO₂ on LiTaO₃ (a) after pretreatment at 673 K, and then (b) after adsorption of CO₂ and evacuation at room temperature.

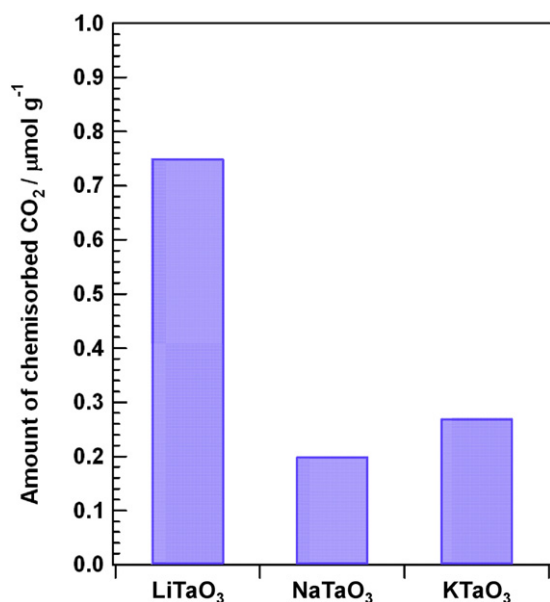


Fig. 7. Amount of chemisorbed CO₂ on ATaO₃ (A = Li, Na, K).

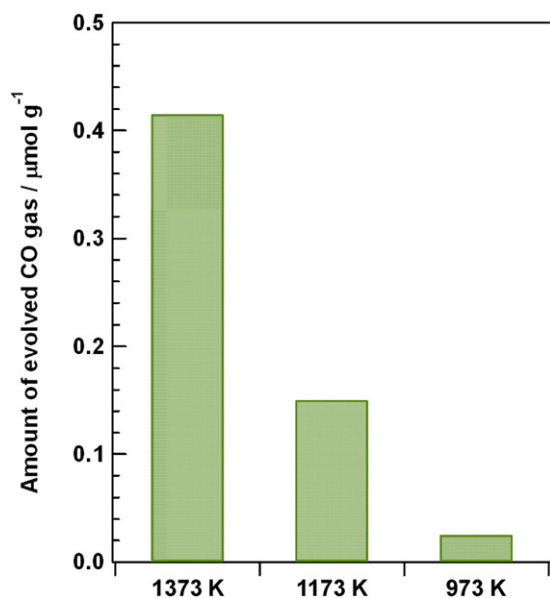


Fig. 8. Amount of evolved CO gas for the photocatalytic reduction of CO₂ in the presence of H₂ as a reductant over LiTaO₃ calcined at 1373, 1173, and 973 K after 24 h of photoirradiation.

chemisorbed CO₂ gas over MgO (130 μmol g⁻¹) is enormous as compared to that on LiTaO₃ (0.75 μmol g⁻¹) [12,13]. Accordingly, the photoactive site of LiTaO₃ would be able to reduce adsorbed CO₂ to CO under photoirradiation effectively. We speculate that a smooth charge separation in LiTaO₃ contributes to the effective photocatalytic reduction of CO₂ in the presence of H₂. Generally, the high crystallinity of photocatalyst is known to provide the smooth charge separation. In our case, the photocatalytic activity increased with increasing the calcination temperature of LiTaO₃ despite decreasing the specific surface area as shown in Fig. 8. The BET specific surface areas of LiTaO₃ calcined at 973, 1173, and

1373 K are 1.1, 0.77, and 0.28 m² g⁻¹, respectively. On the other hand, all peaks in the XRD pattern of LiTaO₃ became sharper and higher with increasing the calcination temperature. In this study, we found that some compound oxides such as ATaO₃ (A = Li, Na, K) exhibit the photocatalytic activity for the photocatalytic reduction of CO₂ in the presence of H₂ and expanded the capability of the effective CO₂ photocatalytic reduction system using high crystallinity of LiTaO₃; however the observed activity is very low. High specific surface area of LiTaO₃ is now under investigation and preparation.

4. Conclusion

It is found that photocatalytic reduction of CO₂ using H₂ as a reductant proceeds over ATaO₃ (A = Li, Na, K). CO gas was evolved over all ATaO₃ (A = Li, Na, K) samples under photoirradiation and the other compounds were not produced in the gas phase. LiTaO₃ exhibits the highest activity in the ATaO₃ (A = Li, Na, K) samples. The photocatalytic activity was higher in the order corresponding to KTaO₃, NaTaO₃ and LiTaO₃ (LiTaO₃ > NaTaO₃ > KTaO₃). The order of the photocatalytic activities was consistent with that of the *E_g* (optical gap) values. Amount of evolved CO gas almost depends on amount of chemisorbed CO₂ in the case of ATaO₃. The photoactive site of LiTaO₃ would be able to capture CO₂ in the gas phase and reduce the adsorbed CO₂ to CO under photoirradiation effectively as compared to that of NaTaO₃ and KTaO₃.

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